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RESEARCH MEMORANDUM

EFFECT OF FREE METHYL RADICALS ON SLOW

OXIDATION OF PROPANE AND ETHANE

By Glen E. McDonald and Rose L. Schalla

Lewis Flight Propulsion Laboratory

Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
WASHINGTON
August 28, 1952

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SUMMARY

A study of the effect of free methyl radicals on the slow oxidation of both ethane and propane was made by means of a photochemical decomposition reaction in a static system. The introduction of methyl radicals into a mixture of propane and oxygen or ethane and oxygen substantially lowered the initiation temperature of the combustion of the hydrocarbon. Measurements were made of the amount of propane oxidized in the presence of free methyl radicals at temperatures ranging from 0° to 116° C and for two different concentrations of propane. Oxidation of ethane, which was induced by the free methyl radical, was investigated for only one concentration from 0° to 183° C.

From a plot of the log percentage of propane oxidized against the reciprocal temperature (°K), a zero activation energy was found for the reaction below 40° C. For ethane the activation energy was zero below 120° C. Above these two temperatures an increase in the activation energy was observed. A mechanism is proposed to account for the zero activation energy, but no attempt was made to interpret the higher temperature reactions.

INTRODUCTION

In recent years considerable attention has been directed toward investigating the role that active particles play in combustion reactions. Tanford and Pease (reference 1) developed a mechanism of flame propagation in which they placed considerable emphasis on the importance of hydrogen atoms. Geib and Harteck (reference 2) showed that the introduction of hydrogen atoms into a mixture of methane and oxygen would induce a very rapid reaction at temperatures as low as -183° C. The slow oxidation of methane would otherwise not occur below 300° C. These and other studies have demonstrated that hydrogen atoms have a great influence on combustion reactions. However, the effects of other active particles formed during the combustion of hydrocarbon fuels have received practically no investigation. Therefore, as part of the fundamental combustion program at the NACA Lewis laboratory a study was undertaken to observe

the effects of another active particle, namely the free methyl radical, on slow combustion reactions. Reference 3, the only other investigation of this subject, reported the reaction of free methyl radicals with an oxygen-methane mixture.
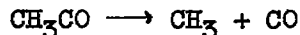
The purpose of this investigation is to extend the study of the effect of free methyl radicals on a hydrocarbon oxidation reaction by using propane and ethane as the hydrocarbons. In the case of ethane the free methyl radicals were produced by the photochemical dissociation of acetone in the presence of ethane and oxygen. For the propane work both acetone and azomethane were used as a source of free methyl radicals. Trotman-Dickenson and Steacie (reference 4) cite numerous advantages of using acetone as a source of free methyl radicals. Perhaps one of the more important reasons for its selection was that the mechanism of the photochemical dissociation of acetone has been extensively investigated (pp. 200-221, reference 5). The initial step has been established to be
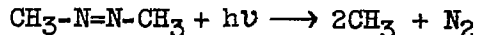
$$CH_3COCH_3 + h\nu \longrightarrow 2CH_3 + CO$$
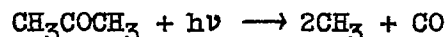
Possibly at temperatures below 40° C

$$CH_3COCH_3 + h\nu \longrightarrow CH_3CO + CH_3$$

then followed by

$$CH_3CO \longrightarrow CH_3 + CO$$

While azomethane was a less convenient source, its dissociation has been studied (reference 6) and reported to proceed as follows:

$$CH_3-N=N-CH_3 + h\nu \longrightarrow 2CH_3 + N_2$$

The research reported here was directed toward finding the minimum practical temperature at which a propane oxidation and an ethane oxidation reaction could be initiated by free methyl radicals, and toward establishing an activation energy for such a reaction. In addition, an attempt was made to postulate the most probable mechanisms that the reactions followed.

APPARATUS AND PROCEDURE

Materials. - Azomethane was obtained by first preparing dimethylhydrazine dihydrochloride according to the method of Hatt described in reference 7. The oxidation of the dimethylhydrazine dihydrochloride and subsequent purification was carried out by the method described by Diels and Koll (reference 8). Mallinckrodt analytical reagent grade acetone was used without further purification. Matheson Company extra pure (99.9 percent) propane, Ohio Chemical and Manufacturing Company ethane, and commercial oxygen were also used without further purification.

Method. - A diagram of the apparatus used in this work is shown in figure 1. The photolysis of acetone in an ethane-oxygen and propane-oxygen mixture and the photolysis of azomethane in the propane-oxygen mixture were carried out in a 393.5-milliliter quartz reaction vessel (E). The reaction vessel was submerged in a constant-temperature oil bath maintained at ±0.5° C of the desired temperature. Directly above the reaction vessel was a quartz lens (G) used to collimate the light rays emitted by a General Electric B-H6 lamp (F). This B-H6 lamp emitted light from approximately 2300 angstroms into the visible wavelength region. Light of such wavelength was capable of dissociating acetone and azomethane but not sufficiently short to dissociate ethane, propane, or oxygen.

To make certain that a hydrocarbon-oxygen mixture was in no way being affected by the ultraviolet light used for dissociating the acetone or azomethane, a mixture of propane and oxygen of known concentration was irradiated by the B-H6 lamp for several hours. In the ensuing analysis all of the propane was found to be still present. Total recovery of the propane was also proof against any mercury photosensitized reaction. To ensure a uniform intensity for each experiment a new B-H6 lamp was used for each run.

The storage bulb (A) contained the hydrocarbon, oxygen, and acetone or azomethane mixture. A volume of this mixture equivalent to a pressure of approximately 220 millimeters of mercury was admitted to the reaction vessel and irradiated until all the acetone or azomethane was dissociated. From infrared spectra (figs. 2 and 3) it was found that 5 hours were sufficient to dissociate all of the acetone. Since azomethane absorbs at longer wavelengths than acetone, it was more quickly dissociated by the B-H6 lamp and consequently was also completely dissociated in 5 hours. Hence all data were reported after 5 hours of photolysis.

Analysis for unreacted ethane or propane. - After the mixture had been photolysed, the reaction products were pumped out of the reaction vessel through an Ascarite trap (I, fig. 1) to remove the carbon dioxide and then through a still (J) which was cooled to liquid nitrogen

temperature. The condensable products, including any unreacted propane
or ethane, were frozen out in this still. The oxygen, carbon monoxide,
and other noncondensable products passed through and were exhausted from
the pump. The inner trap of the still was wound with resistance wire so
that it could be heated while remaining in the liquid nitrogen bath.
The heating of the still was controlled by a Variac transformer which
was so adjusted that the temperature of the still was great enough to
produce a 0.25-millimeter vapor pressure of propane or ethane when meas-
ured by a McLeod gage (K). This setting was determined by using samples
of pure propane and ethane and noting the vapor pressure at various
temperatures. Since no substance in the condensed products had a higher
vapor pressure than propane or ethane, the temperature required to pro-
duce a 0.25-millimeter pressure of the hydrocarbon was not great enough
to cause any significant vapor pressure from any of the other condensable
products. Carbon dioxide, which does have a vapor pressure equal to that
of propane, had already been removed by the Ascarite trap.

The hydrocarbon that had been vaporized by heating the still was
recondensed by a liquid nitrogen bath in a measuring tube (L) of known
volume. A mercury leveling bulb (M) attached to this measuring tube was
used to determine the pressure of the propane or ethane collected in the
tube. Another trap of Ascarite (I') was added to the apparatus so that
the gas collected in the measuring tube could be transferred to the
Ascarite and then back to the measuring tube again by applying liquid
nitrogen baths. This additional trap of Ascarite made certain that any
carbon dioxide which went through the first Ascarite trap was removed
before the final pressure of the hydrocarbon was recorded. From blank
runs in which a known concentration of pure propane was admitted to the
reaction vessel and then analyzed, the experimental accuracy was found
to be within ±2.0 percent.

From the pressure, temperature, and volume of the unreacted hydro-
carbon collected in the tube as well as from the temperature and volume
of the original reaction vessel, the amount of unused hydrocarbon could
be determined. From an analysis made of the gases in the storage bulb,
the amount of hydrocarbon initially present was known. The difference
between the original amount and the amount recovered was a measure of
the propane or ethane used.

Qualitative analysis of reaction products. - As a qualitative
analysis of the reaction products, some mixtures after photolysis were
admitted directly to an evacuated infrared cell. An infrared spectrum
of the reaction products was then obtained by means of a Baird self-
recording infrared spectrophotometer. The presence of peroxides in the
degassed condensate from the reaction vessel was ascertained with ferrous
sulfate.

RESULTS

The results of subjecting a mixture of approximately 2 parts propane, 2 parts acetone, and 18 parts oxygen, as well as a mixture of $1\frac{1}{2}$ parts propane, 2 parts acetone, and 18 parts oxygen to photolysis are shown in tables I and II, respectively. In each table are found the temperature ($^\circ$C) and the reciprocal temperature ($^\circ$K) at which each propane, acetone, and oxygen mixture was photolysed. The pressure of the propane initially present for each run and the pressure of the propane recovered after photolysing the mixture are also given. From the difference between these two quantities, the percentage of propane oxidized was calculated. The quantum yield for propane oxidation is proportional to the percentage of propane oxidized. In the last column are the values of the pressure change observed for each run. Table III is a similar table for a mixture of 2 parts ethane, 2 parts acetone, and 18 parts oxygen.

Although the minimum temperature at which free methyl radicals could initiate the oxidation of propane or ethane was being sought, no runs were made below 0° C because of the difficulty of obtaining lower reaction-vessel temperatures and the possibility of condensation of the acetone. Since Pease (reference 9) has shown that no appreciable reaction takes place between a 50-50 mixture of oxygen and propane below 250° C, the fact that with the presence of free methyl radicals the initiation temperature is somewhere below 0° C indicates the strong oxidation-promoting effect exerted by free methyl radicals. In figure 4 are shown plots of log percentage of propane oxidized against the reciprocal temperature ($^\circ$K) from tables I and II. In figure 5 is a similar plot for the ethane data. As can be observed from figure 4, the quantum yield for propane oxidation is independent of temperature below 40° C. For ethane the amount of reaction is independent of temperature below 120° C. Since there is some evidence in the literature that the dissociation of acetone at lower temperatues is taking place in two stages, the photolysis of azomethane was used as an alternative source of free methyl radicals to check the lower temperature curve for propane. The results of this work are shown in table IV and figure 6. It is further established by figure 6 that for propane the amount of reaction below 40° C was temperature independent. The photolysis of azomethane in the presence of propane and oxygen was repeated with a Corning 5874 filter between the B-H6 lamp and the reaction vessel. This filter prevented the transmission of light of wavelengths shorter than 3100 angstroms. Since the maximum absorption band for azomethane is between 3400 and 3500 angstroms, its dissociation was not affected. The results of this work showed that the amount of reaction was temperature independent from 0° to 112° C, the latter being the highest temperature investigated. No quantum yield can be calculated for the sloping portion of the curve, since the exact nature and concentration of the material which causes the additional reaction is not known.

As an aid in explaining the mechanisms which might account for these reactions, qualitative analyses were made of the reaction products by use of infrared spectra (figs. 7 to 9). The results of the infrared spectra analyses for all experiments except the one in which a filter was used were as follows:

(1) Appreciable quantities of methyl formate were found at low temperatures. The amount decreased gradually with increasing temperature.

(2) Methyl alcohol was found in small quantities at low temperatures but increased greatly with increasing temperature.

(3) Carbon dioxide was present in about equal concentration at all temperatures.

(4) Carbon monoxide was present at all temperatures, but increased with increasing temperature.

(5) Water was found at all temperatures.

(6) No ethane was found in the products of the propane oxidation when either acetone or azomethane was used.

Special checks were made of the spectra for such compounds as formaldehyde, formic acid, acetic acid, and acetaldehyde, but no bands could be found for these compounds. All of these compounds are dissociated by ultraviolet light and therefore may have been photochemically dissociated if they were formed. Stable peroxides of a type that have the general reactions of hydrogen peroxide were shown to be present by tests with ferrous sulfate on a liquid condensate from the reaction.

DISCUSSION OF RESULTS

A mechanism which would explain the photochemical oxidation of propane should account for the fact that the reaction occurs at a temperature as low as 0° C, whereas a thermal oxidation of propane does not proceed below 200° C. This difference between the temperature thresholds for the reactions suggests that the products of the acetone photolysis are responsible for the initiation of the propane photo-oxidation. The primary process in the acetone photolysis is the formation of a free methyl radical (reference 10). However, it does not appear that the reaction is between a methyl radical and propane because, in contrast to the ease of reaction observed in these experiments, the reaction of a methyl radical with propane has a relatively slow rate at the temperatures used in these experiments (p. 520, reference 5).

Moreover, it has been shown in reference 11 that the reaction of a methyl radical in the presence of oxygen is the formation of a methylperoxy radical. The absence of any ethane formed in the experiments with propane also confirms that the primary reaction of the methyl radical in the presence of the high oxygen concentration used in these experiments is this formation of a methylperoxy radical. Thus, any interpretation of the secondary reactions leading to the oxidation of propane is dependent on the knowledge of the reactions of the methylperoxy radical.

It is suggested that the reaction which accounts for the oxidation of the propane is the reaction of the propane with this methylperoxy radical

$$CH_3O_2 + C_3H_8 = Products$$
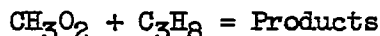
It is assumed that this elementary reaction may represent the over-all reaction for the disappearance of propane, because propane is not considered to be formed by any reaction. Nor is it presumed to disappear by any reaction other than the one given. Under these limiting conditions one net reaction may be written. The over-all rate law may then be used to determine the nature of this reactive intermediate which is produced by the absorption of light. Because of the complexity of the reaction products which result from the propane oxidation, it is not possible to propose the successive steps of a complete mechanism for the oxidation.

Although propane is not presumed to enter any other reactions, the methylperoxy radicals may disappear by reactions other than combination with propane. The alternative reaction proposed for the methylperoxy radical is decomposition to a formyl radical and water. This reaction has been studied by Marcotte and Noyes (reference 10) and determined to have an activation energy of zero. The rate of disappearance of propane is given by the expression

$$-\frac{d(C_3H_8)}{dt} = k_1 (CH_3O_2) (C_3H_8)$$

The rate of disappearance of the methylperoxy radical by decomposition is given by the expression

$$-\frac{d(CH_3O_2)}{dt} = k_2 (CH_3O_2)$$

The relative rates of these two reactions in terms of quantum yields is given by

$$\frac{C_3H_8 \text{ oxidized}}{H_2O \text{ formed}} = \frac{k_1}{k_2} (C_3H_8)$$

Since the concentration of a radical does not occur in the expression, the results are not affected by the photolysis of all of the acetone.

The effect of the propane pressure on the rate of reaction was investigated by photolysing the acetone with different pressures of propane. The quantum yield for propane oxidation changes only 2 percent for a 20-percent change in the pressure of propane. This indicates that the rate of reaction is independent of the change in propane pressure of a magnitude equal to that encountered during the course of the oxidation. The ratio of the quantum yields is the ratio of the rates of reaction. The difference in activation energy is the variation in the relative amount of reaction with temperature.

Since the rate of decomposition of the methylperoxy radical is independent of temperature, then for these experiments at different temperatures, the variation with temperature of the specific reaction-rate constant for the oxidation of the propane is proportional to the change in the amount of propane oxidized:

$$\text{Percentage } C_3H_8 \text{ oxidized} \approx k_1$$

The results are independent of the possible formation of water by any other mechanism, such as the thermal decomposition of hydroperoxides (reference 12), which would complicate a complete photochemical mechanism.

The results of these experiments show that the amount of propane oxidation is independent of temperature below 40° C and that the amount of ethane oxidation is independent of temperature below 120° C. This zero slope for the lower curve indicates that the activation energy for that region must be very small. Therefore the reaction which represents the oxidation of either propane or ethane in the presence of free methyl radicals has a low activation energy.

In general, in determining the activation energy for the oxidation of propane, the only manner by which the rate of photo-oxidation of propane could be temperature independent and still not be zero would be for the reaction of oxidation to have an activation energy exactly equal to the activation energy for the competing reaction. The probability of occurrence of this situation is small. Moreover, the fact that the rate is sufficiently fast to oxidize the propane at a temperature of 0° C points to a low activation energy for the elementary reaction.

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In addition, it is plausible that the activation energy is low in the reaction of the methylperoxy radical because the reactions might be analogous to the general reactions of the HO_2 radical. This radical has been found by Geib and Harteck (reference 2) to have a zero activation energy for the oxidation of various substances. Furthermore, the selection of the particle which has this low energy of activation is simplified because several other particles which may be present in the reaction require a larger energy of activation for reaction with hydrocarbons than that observed in the present experiments. The active particles which might be considered for such a reaction are hydroxyl, oxygen atom, methoxy, and HO_2. Avramenko and Lorentso (reference 12) have found that the activation energy for the reaction of hydroxyl with ethane is 5.5 kilocalories per mole. Although the activation energy for the reaction of the hydroxyl with propane would be expected to be slightly lower, it would seem that it would be at least 2 kilocalories per mole. Consequently the hydroxyl radical and the analogous radical, CH_3O, methoxy, are not considered to be the substances attacking propane or ethane. The exclusion of the methoxy radical is substantiated by the results of reference 11 in which no oxidation of ethane was observed in the presence of methoxy radicals at a temperature of 140° C. Harteck has reported in reference 5 (p. 521) that oxygen atoms have an activation energy of 7 kilocalories per mole for reaction with ethane; therefore the reaction of oxygen atoms with propane or ethane is believed not to occur. The HO_2 particle, which is reactive enough to explain the results obtained in these experiments, is not formed in an appreciable quantity by any reaction occurring in the system.

The sloping portion of the curve for both the propane and the ethane oxidations probably results from the reaction of the hydrocarbon with a particle produced by the photochemical dissociation of some compound formed during the oxidation reaction. No calculation can be made for the sloping portion of the curve. Ethane required a higher temperature for this additional reaction than did propane. Since the sloping portion was not obtained up to 112° C with propane when a filter was used to cut off the light below 3100 angstroms, it appears that the additional reaction was the result of the decomposition of some compound absorbing below 3100 angstroms. Many carbonyl compounds would fall into this class. However, infrared spectra of the reaction products were not able to reveal any information which would identify the exact source of the reaction.

Although a complete mechanism for photo-oxidation has not been postulated, several reactions may be proposed for the formation of the products observed in the infrared spectra. The initial attack of the methylperoxy radical on the hydrocarbon probably results in the formation of methyl hydroperoxide. The decomposition of the methyl hydroperoxide leads to the formation of formaldehyde and water (reference 13):

$$CH_3OOH \longrightarrow HCHO + H_2O$$
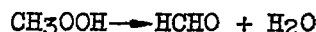
Since formaldehyde would be expected to be oxidized readily, it may possibly react with methylperoxy to form methyl formate:

$$CH_3O_2 + HCHO \longrightarrow CH_3OCOH + OH$$
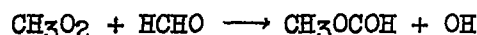
An alternative method of forming methyl formate would also involve the formation of methyl hydroperoxide:

$$CH_3O_2 + HCHO \longrightarrow CH_3OOH + CHO$$
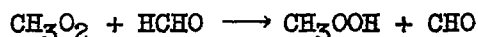
The combination of the methoxy radical (from the decomposition of the methyl hydroperoxide) and the formyl radical would yield methyl formate:

$$CH_3O + CHO \longrightarrow CH_3OCOH$$
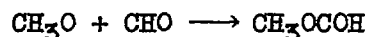
These are suggestions to account for the methyl formate. Any method for the formation of methyl formate directly from formyl radicals must also consider the competing reaction of oxidation:

$$HCO + O_2 \longrightarrow CO_2 + OH$$
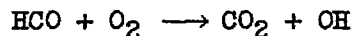
This may indeed partly explain the decrease in the yield of methyl formate with increasing temperature. The higher concentration of methoxy radicals would then be disproportionate by the method proposed in reference 11:

$$CH_3O + CH_3O \longrightarrow CH_3OH + H_2CO$$
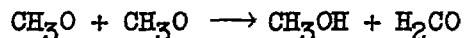
SUMMARY OF RESULTS

· From a study of the effect of free methyl radicals on the slow oxidation of ethane and propane, the following results were obtained:

1. The introduction of free methyl radicals into a propane-oxygen or ethane-oxygen mixture substantially lowered the initiation temperature of the reaction.

2. A plot of the log percentage of propane oxidized against the reciprocal temperature ($^\circ$K) showed the reaction to be independent of temperature below 40° C. A similar plot for ethane showed that reaction to be independent of temperature below 120° C.

3. The activation energy of the free radical oxidation of propane or ethane was therefore low at the lower temperatures.

4. It is proposed that the reaction accounting for the oxidation of either ethane or propane is the reaction of the hydrocarbon with methylperoxy.

5. At higher temperatures an additional reaction set in which was not apparent at lower temperatures.

Lewis Flight Propulsion Laboratory
    National Advisory Committee for Aeronautics
        Cleveland, Ohio, June 25, 1952

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TABLE I - PROPANE ANALYSIS FROM A PHOTOLYSED MIXTURE OF 2 PARTS

PROPANE, 2 PARTS ACETONE, AND 18 PARTS OXYGEN

Temperature (^{o}C)	Reciprocal temperature $\left(\dfrac{1}{^{o}K}\right)$	Propane initially present (mm)	Propane recovered (mm)	Propane oxidized (percent)	Propane oxidized (log percent)	Pressure change (cm)
0.0	3.66×10^{-3}	18.7	15.3	18.2	1.260	-4.0
0.0	3.66	18.7	15.5	17.1	1.233	-4.0
26.5	3.34	18.7	15.5	17.1	1.233	-1.4
39.0	3.21	18.8	15.6	17.0	1.230	0.0
52.0	3.08	18.7	14.9	20.3	1.307	1.4
54.0	3.06	18.7	15.0	19.8	1.297	1.4
65.2	2.96	18.7	14.6	21.9	1.340	2.0
74.7	2.88	18.8	13.6	27.7	1.442	2.1
95.8	2.71	17.3	12.3	28.9	1.461	2.5
116.0	2.57	18.7	12.0	35.8	1.554	3.6

TABLE II - PROPANE ANALYSIS FROM A PHOTOLYSED MIXTURE OF $1\frac{1}{2}$ PARTS

PROPANE, 2 PARTS ACETONE, AND 18 PARTS OXYGEN

Temperature (^{o}C)	Reciprocal temperature $\left(\dfrac{1}{^{o}K}\right)$	Propane initially present (mm)	Propane recovered (mm)	Propane oxidized (percent)	Propane oxidized (log percent)	Pressure change (cm)
0.0	3.66×10^{-3}	13.4	10.4	22.4	1.350	-4.3
0.0	3.66	12.0	9.0	25.0	1.398	-4.0
10.5	3.53	13.5	10.3	23.7	1.375	-3.5
11.3	3.52	13.5	10.0	25.9	1.413	-3.3
59.0	3.01	13.5	9.5	29.6	1.471	1.4
69.0	2.92	13.5	8.5	37.0	1.568	2.5
93.0	2.73	13.5	6.8	49.6	1.695	2.6
110.0	2.61	13.5	6.1	54.8	1.739	3.0

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TABLE III - ETHANE ANALYSIS FROM A PHOTOLYSED MIXTURE OF 2 PARTS

ETHANE, 2 PARTS ACETONE, AND 18 PARTS OXYGEN

Temperature (°C)	Reciprocal temperature $\left(\frac{1}{°K}\right)$	Ethane initially present (mm)	Ethane recovered (mm)	Ethane oxidized (percent)	Ethane oxidized (log percent)	Pressure change (cm)
0.0	3.66X10⁻³	19.6	15.1	23.0	1.362	-4.0
0.0	3.66	20.0	14.9	25.5	1.407	-4.4
8.5	3.55	20.3	15.6	23.2	1.365	-3.6
9.1	3.54	19.4	15.2	21.6	1.334	-3.8
38.0	3.22	20.4	16.6	18.6	1.270	0.4
43.2	3.16	19.7	14.8	24.9	1.396	0.8
77.0	2.86	20.4	14.6	28.4	1.453	2.1
77.0	2.86	20.4	15.1	26.0	1.415	2.1
77.8	2.85	20.6	14.6	29.1	1.464	---
97.0	2.70	21.0	16.2	22.9	1.360	2.5
137.0	2.44	22.2	14.4	35.1	1.545	---
156.0	2.33	21.4	10.7	50.0	1.699	3.6
184.4	2.18	22.5	0.0	100.0	2.000	5.7

TABLE IV - PROPANE ANALYSIS FROM A PHOTOLYSED MIXTURE OF 2 PARTS

PROPANE, 2 PARTS AZOMETHANE, AND 18 PARTS OXYGEN

Temperature (°C)	Reciprocal temperature $\left(\frac{1}{°K}\right)$	Propane initially present (mm)	Propane recovered (mm)	Propane oxidized (percent)	Propane oxidized (log percent)	Pressure change (cm)
0.0	3.66X10⁻³	16.3	13.8	15.3	1.185	-2.0
23.0	3.37	16.4	13.5	17.7	1.248	-0.4
42.5	3.17	16.4	13.6	17.8	1.233	1.5
48.8	3.11	16.4	12.8	22.0	1.342	1.9
54.5	3.05	16.3	12.7	22.1	1.344	2.5
57.5	3.03	16.4	12.4	24.4	1.387	2.6
60.0	3.00	16.4	10.7	34.8	1.542	2.4
70.0	2.92	16.3	12.3	24.5	1.389	2.4
76.0	2.86	16.3	10.1	38.0	1.580	3.4
84.0	2.80	16.4	9.9	39.6	1.598	4.0

A Gas-mixture storage bulb
B Manometers
C Inlet for gases
D Main heating unit
D' Auxiliary heating unit
E Quartz reaction vessel
F Housing for B-H6 lamp
G Quartz lens
H Thermocouple
I,I' Ascarite traps
J Heated still
K To McLeod gage
L Constant-volume measuring tube
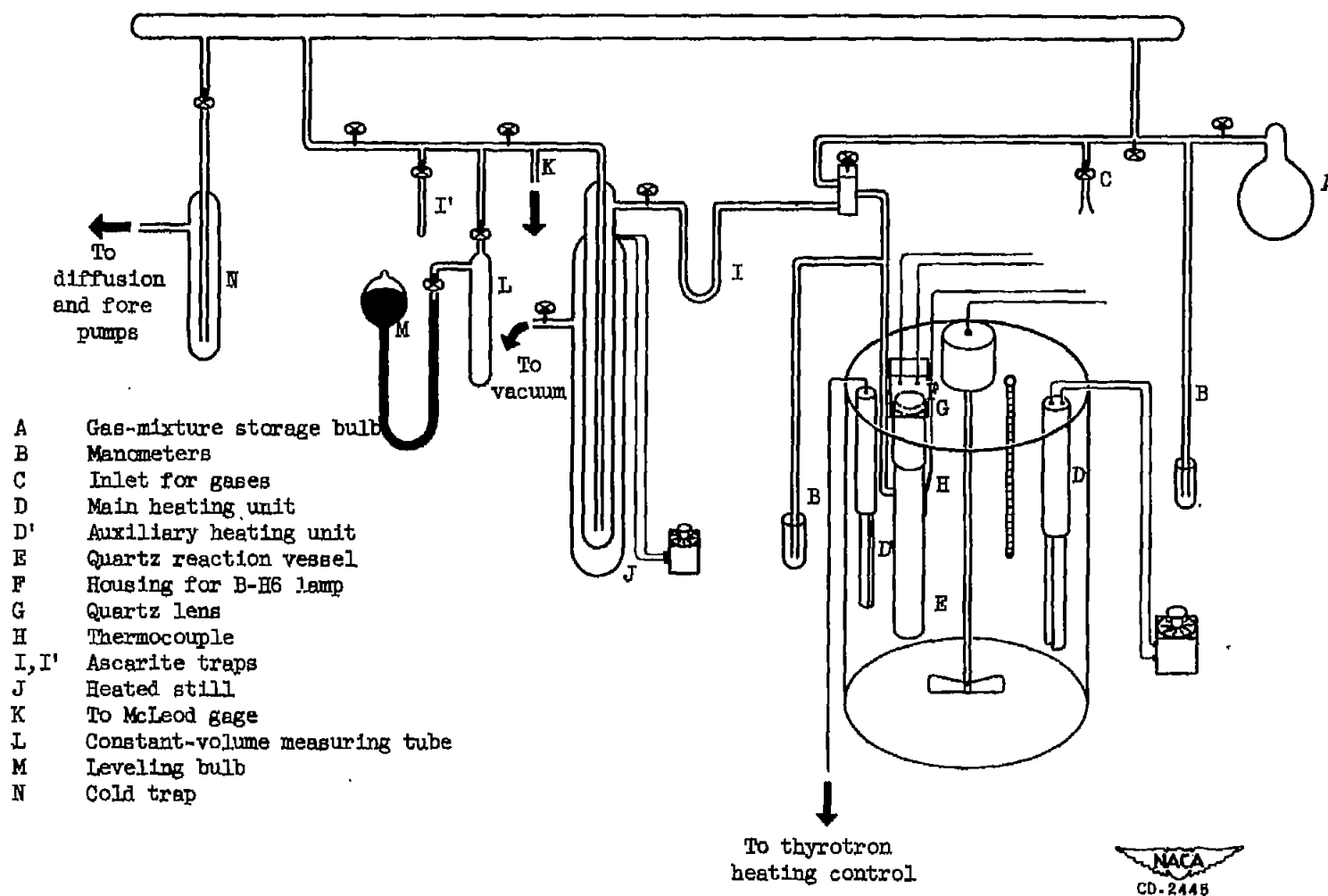M Leveling bulb
N Cold trap

To thyrotron
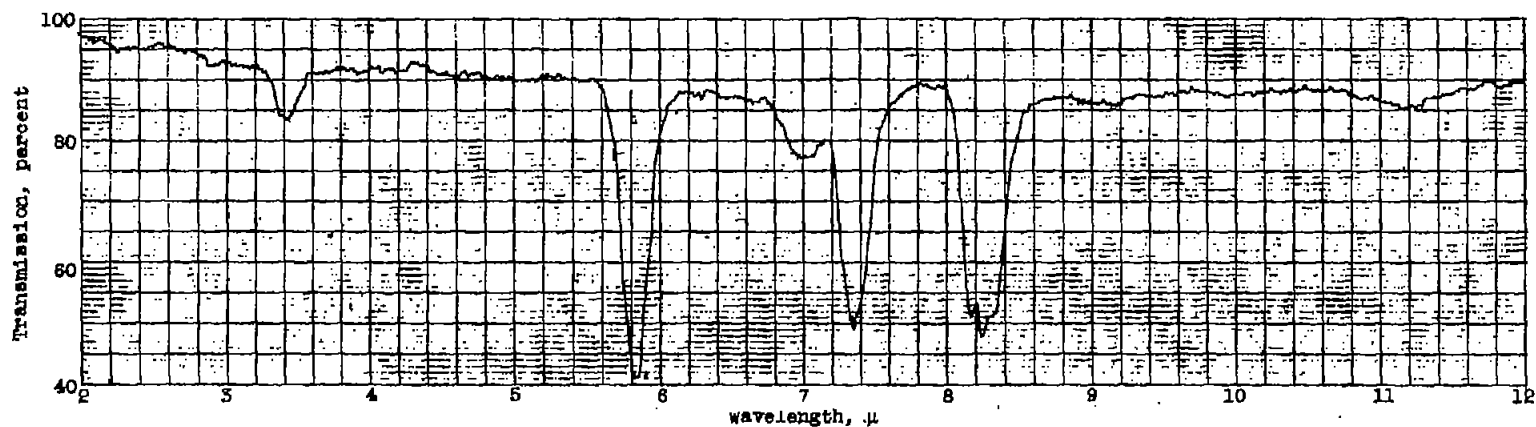heating control

Figure 1. - Diagram of apparatus.
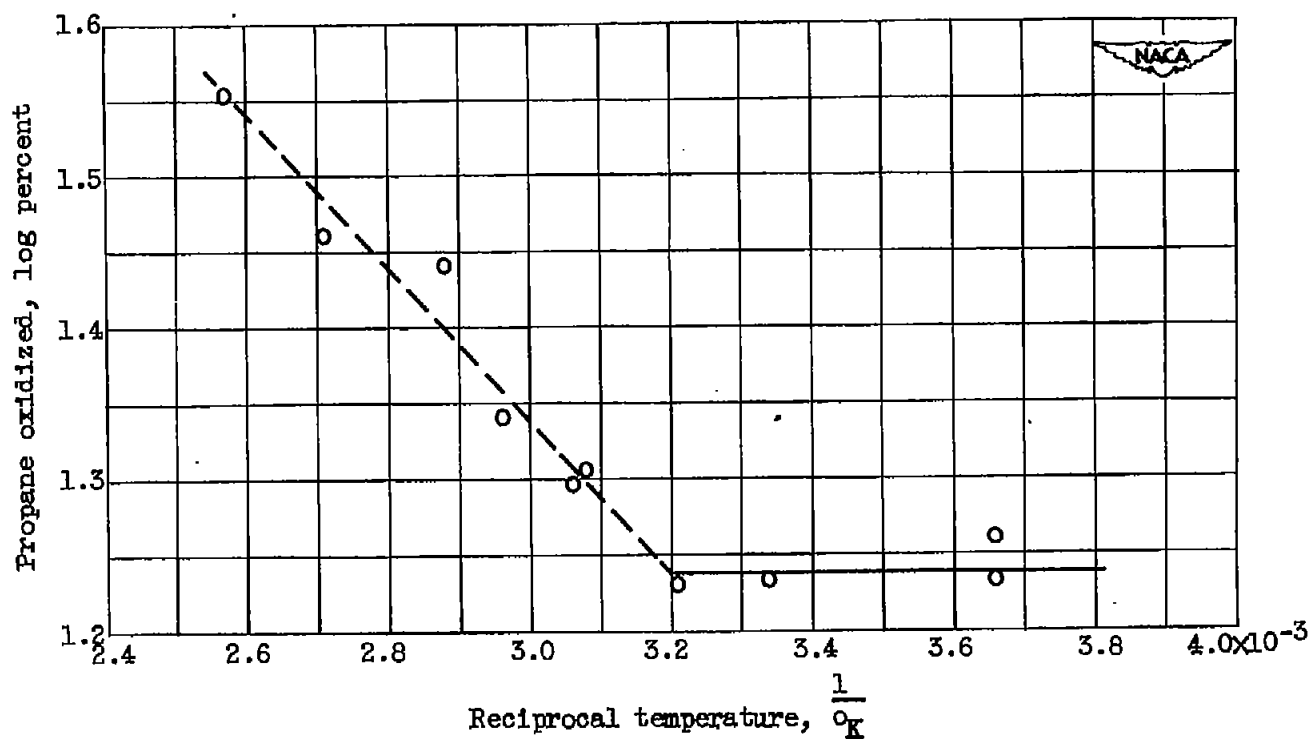
Figure 2. - Infrared absorption spectra of acetone.
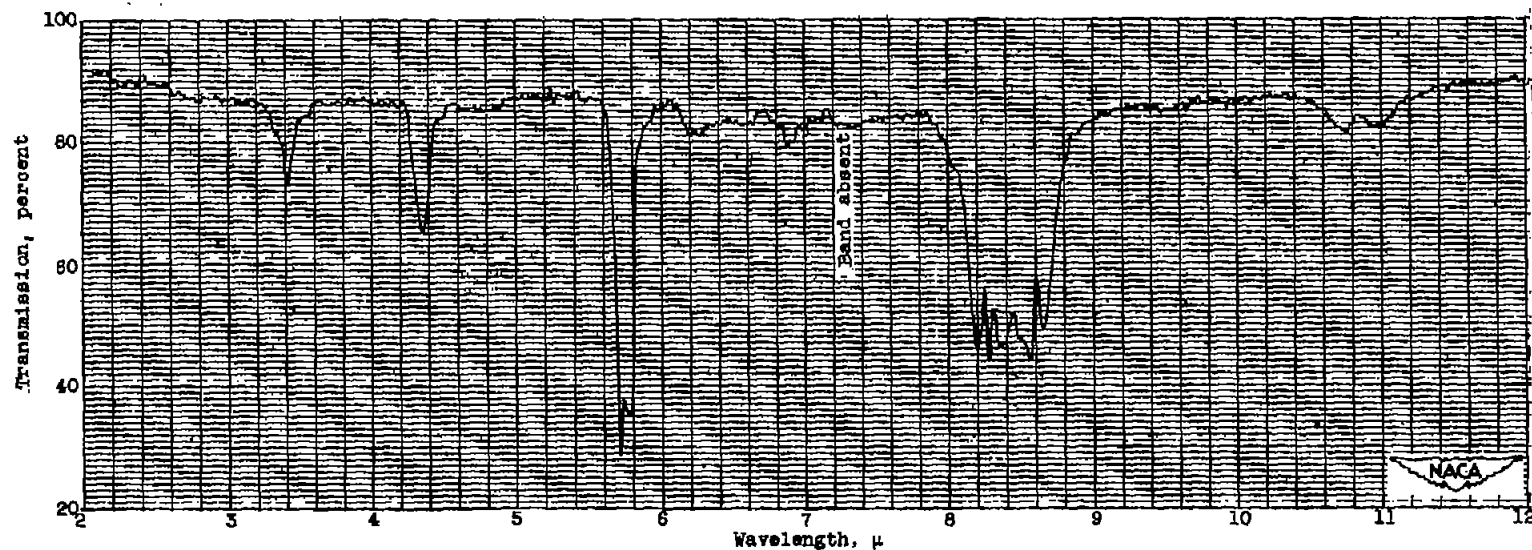
Figure 3. - Infrared absorption spectra of reaction products from mixture of acetone and oxygen photolysed for 5 hours below 40° C. Absence of band at 7.3 microns indicates total dissociation of acetone.

(a) Mixture of 2 parts propane, 2 parts acetone, and 18 parts oxygen.

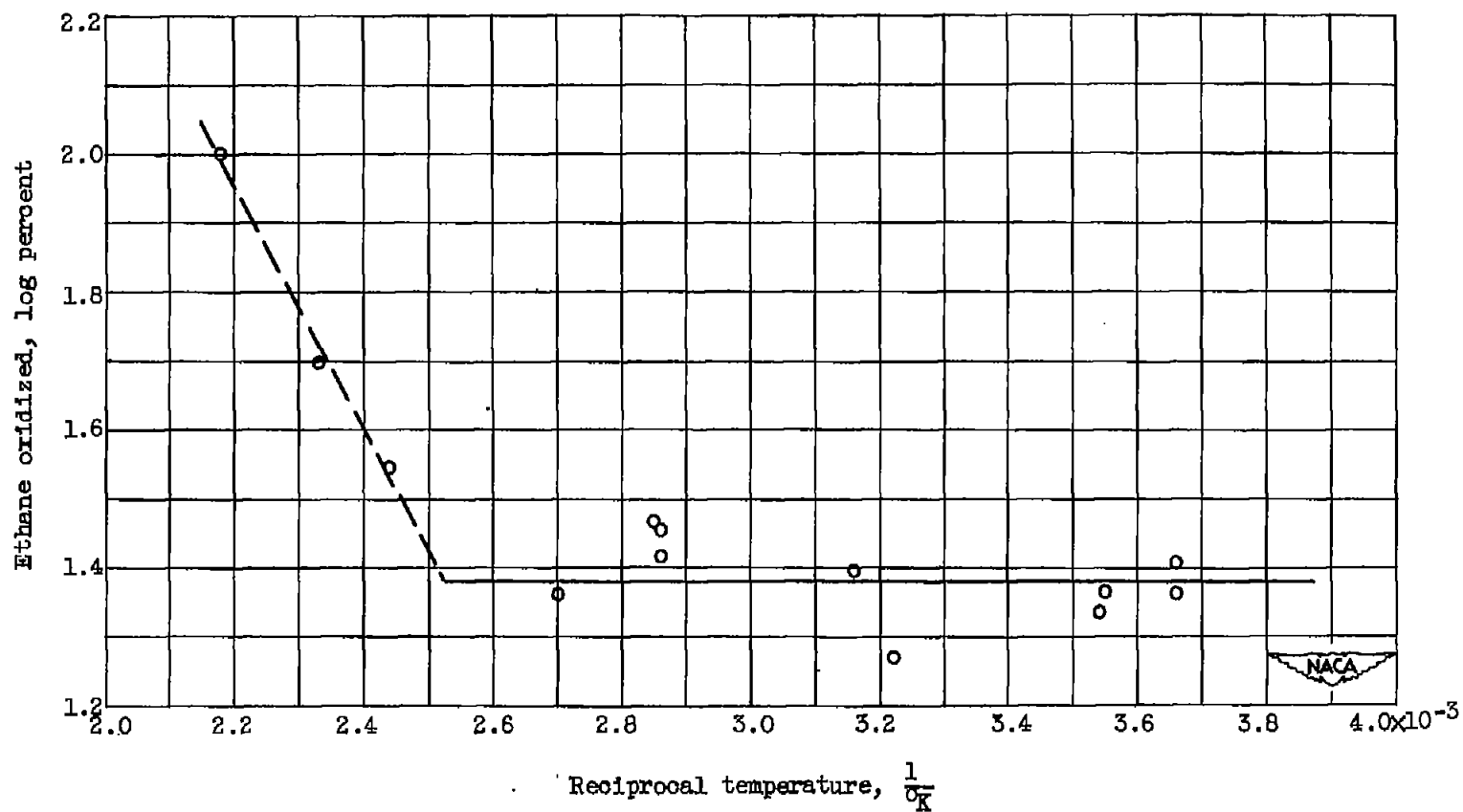Figure 4. - Log percentage of propane oxidized against reciprocal temperature.
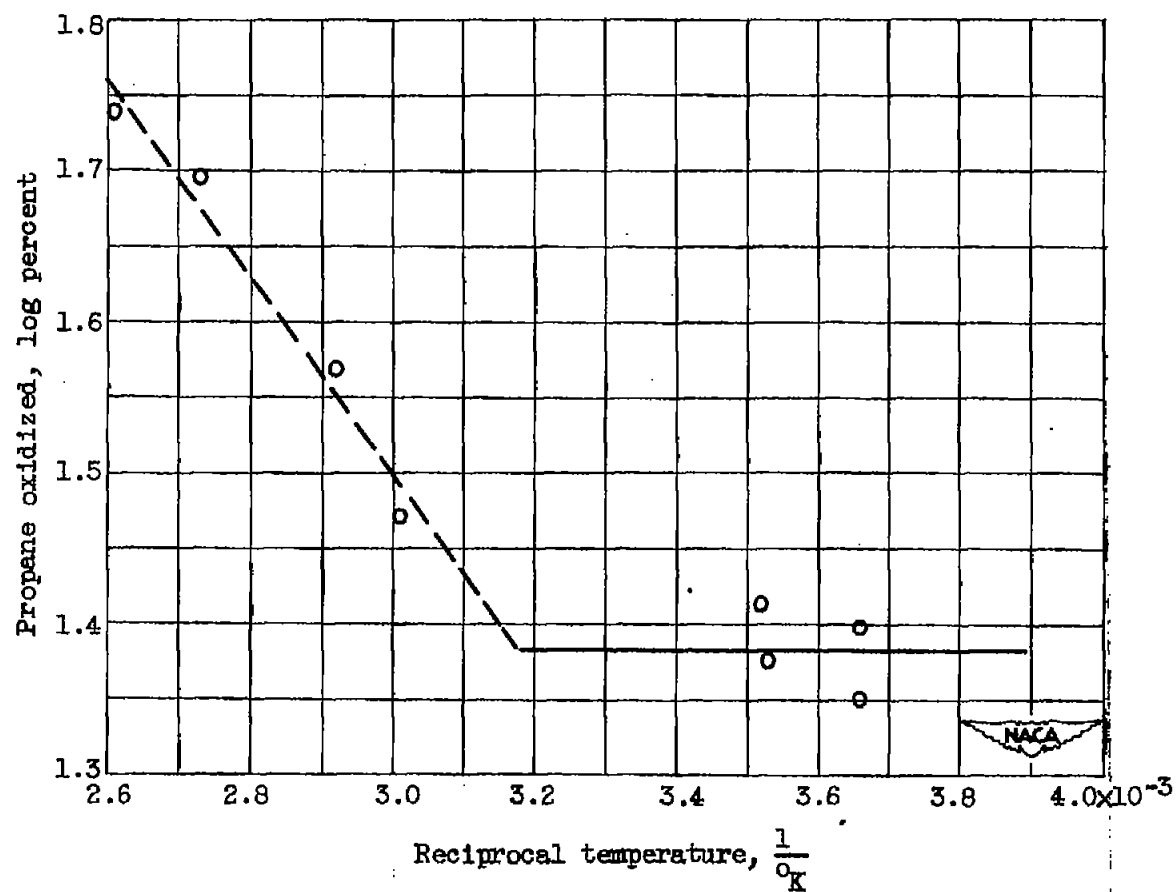
(b) Mixture of $1\frac{1}{2}$ parts propane, 2 parts acetone, and 18 parts oxygen.

Figure 4. - Concluded. Log percentage of propane oxidized against reciprocal temperature.

Figure 5. - Log percentage of ethane oxidized against reciprocal temperature for a mixture of 2 parts ethane, 2 parts acetone, and 18 parts oxygen.
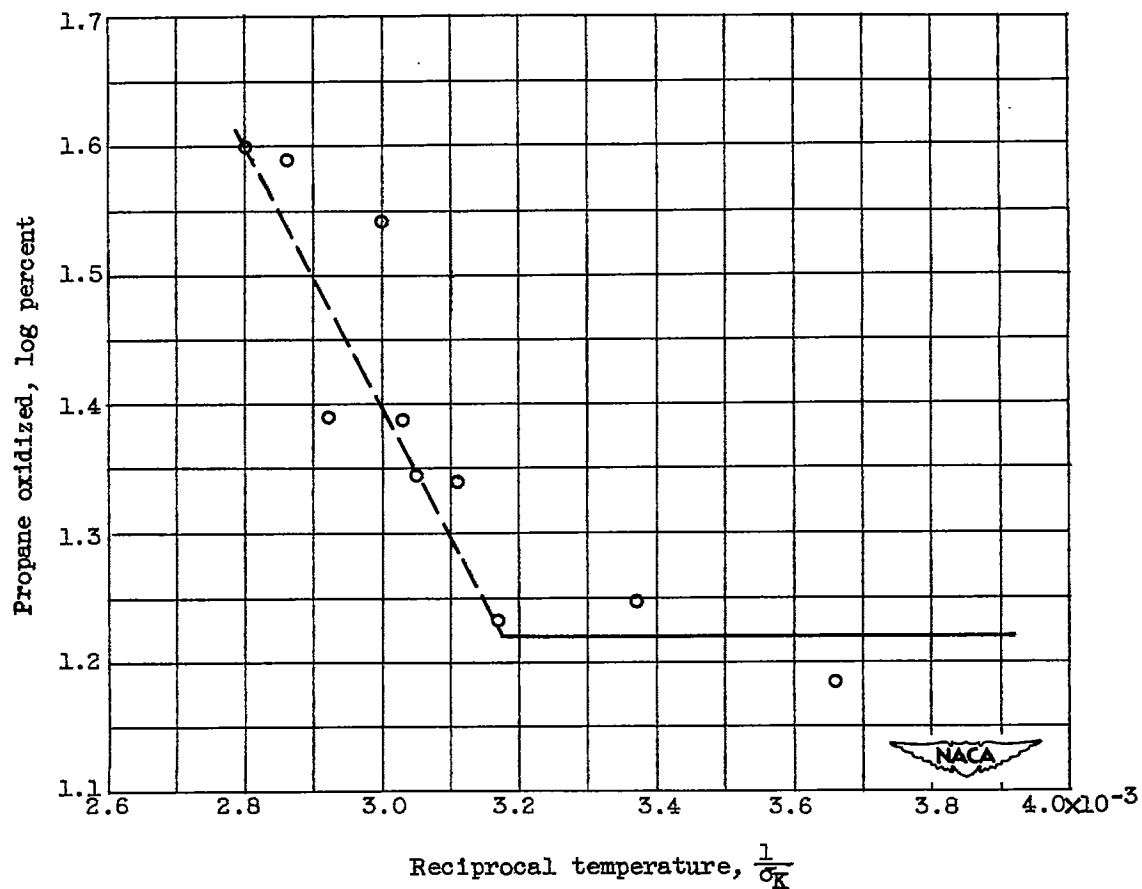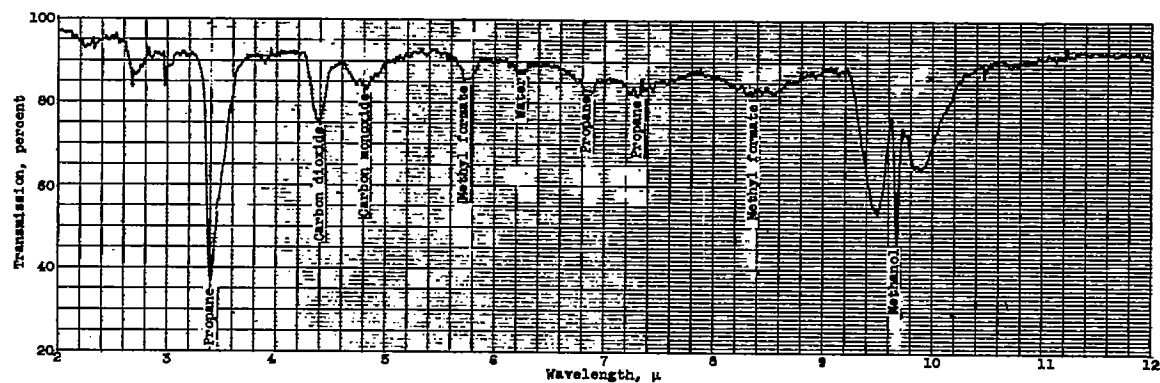
Figure 6. - Log percentage of propane oxidized against reciprocal
    temperature for a mixture of 2 parts propane, 2 parts azomethane,
    and 18 parts oxygen.

Figure 7. - Infrared absorption spectra of reaction products from photolysed mixture of propane, oxygen, and acetone above 40° C.
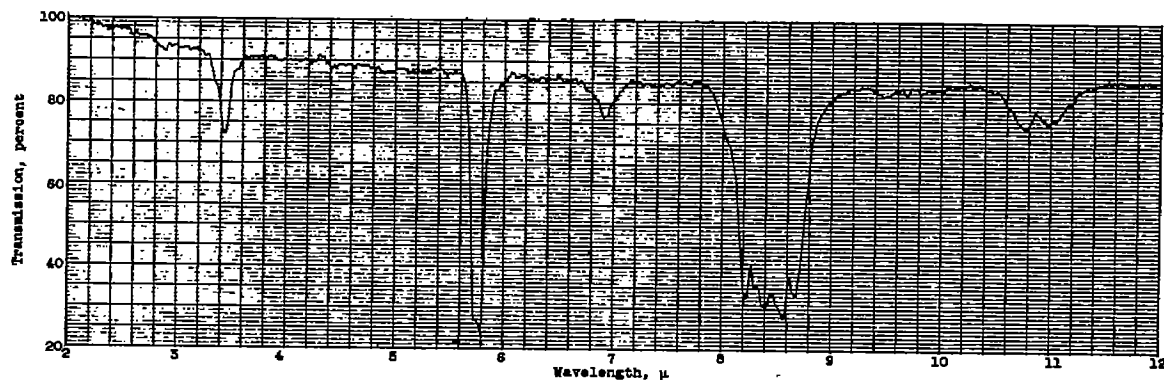

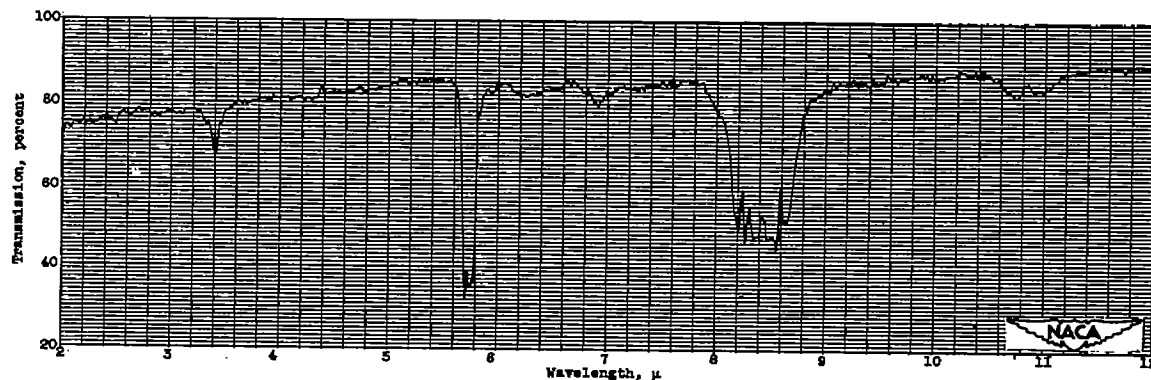Figure 8. - Infrared absorption spectra of methyl formate.

Figure 9. - Infrared absorption spectra of reaction products from mixture of propane, oxygen, and acetone photolysed at 0° C. Propane, carbon dioxide, and products noncondensable in liquid nitrogen are not shown. Except for band for water at 6.28 microns, all bands are for methyl formate.